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ON THE MECHANISM OF SEPARATION OF ETHANOL/WATER MIXTURES BY PERVAPORATION
I. CALCULATIONS OF CONCENTRATION PROFILES*

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Summary

A solution—diffusion model for the permeation of liquid mixtures through polymeric membranes taking into account coupling of fluxes has been developed. The model is applied to the separation by pervaporation of ethanol—water mixtures through cellulose acetate. In order to determine the activities of the permeating components in the polymeric membrane, values of polymer—liquid and liquid—liquid interaction parameters are needed; polymer—liquid interaction parameters have been determined from swelling experiments and liquid—liquid interaction parameters have been calculated from excess free energy of mixing data taken from the literature.

Concentration profiles of water and ethanol in cellulose acetate membranes have been calculated using (a) apparent concentration independent diffusion coefficients, and (b) diffusion coefficients with exponential concentration dependence and two adjustable parameters. It is discussed that the transport of ethanol—water mixtures by pervaporation cannot be explained by using concentration independent diffusion coefficients.

Introduction

Transport of liquids through homogeneous polymeric membranes, as practised during pervaporation, differs from gas separation because the concentrations of the permeating components in the polymer are in general much higher. The high permeant concentrations have, in their turn, a large influence on the diffusion coefficients of the permeants. Hence transport equations derived from gas separation cannot be applied a priori to pervaporation.

For a description of a pervaporation transport model, one should distinguish single component and multicomponent permeability. Single component permeation through homogeneous polymeric membranes can be satisfactorily described by Fick's law with a concentration dependent diffusion coefficient, as has been done by several authors [1—5]. Also, the application of free volume theory to single component permeation [6] shows good agreement between theory and experiment. Paul [7] proposed a model for pressure-

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induced diffusion of liquids through highly swollen rubber membranes, satisfactory agreement between theory and experiment was established.

No satisfactory theory exists that describes the transport of a mixture. Fels [8] tried to modify the free volume concept to include contributions from both penetrants to the total free volume. Although this approach can have a significant contribution to the study of molecular separation phenomena, the agreement between theory and experiment is still lacking.

Greenlaw [9] investigated the effect of a linear relationship between the concentrations of permeants and their diffusion coefficients. For liquid mixtures that behave almost ideally, such as the heptane—hexane mixture used by Greenlaw, this treatment may hold but it is uncertain whether this would be the case for non-ideal mixtures such as ethanol—water.

Tock [10] attempted to predict selectivities for water—dioxane mixtures from permeabilities of the pure components using Fick's law with a concentration dependent diffusion coefficient. Their results show that it would hardly be possible to predict selectivities for non-ideal mixtures from single component permeability data alone.

Lee [11] used a solution—diffusion model with concentration independent diffusion coefficients and without considering a possible coupling of fluxes. As a consequence, the selectivity factor is equal to the ratio of the permeability coefficients obtained from single component permeation experiments. In the case of liquid mixtures which show hardly any mutual interaction, nor any interaction with the polymer, this treatment may hold, but with other mixtures which behave far from ideally, such as ethanol—water, this treatment is probably too simple.

When a liquid mixture permeates through a membrane there will be coupling of fluxes. The flux of a component of the binary mixture may change, not only by the presence of the other component but also by its movement. This phenomenon has been pointed out clearly by Meares [12] in a review article about transport through polymeric membranes from the liquid phase. Coupling can be divided into two parts, a thermodynamic part and a kinetic part. The thermodynamic part, the change in concentration of one component in the membrane due to the presence of another component, is caused by mutual interactions between the permeants in the membrane as well as by interactions between the individual components and the membrane material. The extent of these interactions depends on the polymer—mixed penetrant system. Kinetic coupling is due to the dependence of the concentration on the diffusion coefficients of low molecular weight components in polymers, particularly in glassy polymers. In polymers below their glass transition, such as cellulose acetate, polysulfone and polyacrylonitrile at room temperature, the thermal motions of the chain segments are very much restricted. When low molecular weight components are dissolved in such polymers, the mobility of the chains increases. In the case of a binary mixture, both components will exert a plasticizing effect on the segmental motions, and the mobilities of both permeants will be enhanced by the combined plasticizing action.

Therefore, in a model description for the separation of liquid mixtures by pervaporation, coupling phenomena have to be taken into account.

The object of this article is to present a modified solution–diffusion model which combines both the thermodynamic and the kinetic (diffusive) aspects of the pervaporation process. Our approach differs from the original solution–diffusion model [11, 13, 14] in that we now consider coupling of fluxes, whereas in the original model each component dissolved in the membrane and diffused through it independently. With the model described here it is possible to calculate concentration profiles. When data on experimental concentration profiles are available, it is possible to calculate diffusion coefficients of permeating components in polymeric membranes. In this article we will present calculated concentration profiles of ethanol and water in cellulose acetate membranes using (a) apparent concentration independent diffusion coefficients obtained from steady-state measurements, and (b) diffusion coefficients with an exponential concentration dependence with two adjustable parameters. In a forthcoming article [15] we will report on experimentally determined concentration profiles and discuss these results in terms of the proposed model.

Description of the model

Although the model follows the formalism of the solution–diffusion model some assumptions have been made:

- The model applied to pervaporation processes because only boundary conditions of the pervaporation process are included. In principle the model can be modified to apply to other membrane processes.
- The model describes the flow of permeants in the membrane as a one-dimensional steady-state diffusion: the permeation rate is independent of time and the chemical potential of a component in the membrane is only a function of concentration and distance and not of time. Another important point is that during steady-state the membrane undergoes no structural changes.
- The application of the model is restricted to homogeneous membranes or to very dense toplayers of asymmetric or composite membranes where transport takes place by diffusion and not by convection.
- Transport through the membrane is rate-determining. This assumption implies that surface processes such as sorption at the feed/membrane interface and desorption at the membrane/permeate interface are fast compared to diffusion processes through the membrane.
- The interfaces of the membrane are in equilibrium with the upstream and downstream phase. This means that the chemical potential of component i in the upstream phase is equal to the chemical potential of component i just inside the membrane.
- The chemical potential or activity of a component in the polymeric membrane can be described by Flory–Huggins thermodynamics [16].

Binning [1] was the first to propose that the transport of liquids through homogeneous membranes takes place by a solution—diffusion mechanism.

According to the original solution—diffusion model [13, 14], the flux of a component i through the membrane can be described by the product of concentration, mobility and driving force. The driving force in most membrane processes and also in pervaporation is given by the gradient in the chemical potential. For component i the flux can be described by

$$J_i = -c_i B_i \frac{d\mu_i}{dx} \tag{1}$$

At constant temperature, eqn. (1) may be written as

$$J_i = -c_i B_i \left(RT \frac{d \ln a_i}{dx} + \bar{V}_i \frac{dP}{dx} \right)_T \tag{2}$$

The pressure difference between the upstream and downstream phase is about 1 bar (0.1 MPa) in pervaporation processes. Therefore, the pressure gradient can be neglected with respect to the activity gradient

$$J_i = -c_i B_i RT \frac{d \ln a_i}{dx} \tag{3}$$

Assuming that

$$D_i = RT B_i \tag{4}$$

where D_i is the diffusion coefficient of component i in the polymer-fixed frame of reference, substitution of eqn. (4) in eqn. (3) gives

$$J_i = -c_i D_i \frac{d \ln a_i}{dx} \tag{5}$$

The activity of a component in the membrane can be described by Flory—Huggins thermodynamics [16]. For a binary system the activities a_1 and a_2 are given by

$$\ln a_1 = \frac{\Delta\mu_1}{RT} = \ln v_1 + \left(1 - \frac{V_1}{V_2}\right) v_2 + \chi_{12} v_2^2 \tag{6}$$

$$\ln a_2 = \frac{\Delta\mu_2}{RT} = \ln v_2 + \left(1 - \frac{V_2}{V_1}\right) v_1 + \chi_{12} \frac{V_2}{V_1} v_1^2 \tag{7}$$

χ_{12} is a binary interaction parameter between components 1 and 2 called the Flory—Huggins interaction parameter. This interaction parameter is a dimensionless quantity characterizing the difference in interaction energy of a solvent molecule immersed in pure polymer compared with one in pure solvent.

In the case of a polymeric membrane and a binary liquid mixture, a ternary system, the activities a_1 and a_2 of liquid components 1 and 2 in the polymeric membrane are given by [16]

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) - \phi_2 \frac{V_1}{V_2} - \phi_3 \frac{V_1}{V_3} + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23} \frac{V_1}{V_2} \phi_2\phi_3 \quad (8)$$

$$\ln a_2 = \ln \phi_2 + (1 - \phi_2) - \phi_1 \frac{V_2}{V_1} - \phi_3 \frac{V_2}{V_3} + (\chi_{12}\phi_1 \frac{V_2}{V_1} + \chi_{23}\phi_3)(\phi_1 + \phi_3) - \chi_{13} \frac{V_2}{V_1} \phi_1\phi_3 \quad (9)$$

Substitution of eqns. (8) and (9) into eqn. (5) gives

$$J_1 = -\phi_1 D_1(\phi_1,\phi_2) \frac{d}{dx} \left[\ln \phi_1 + (1 - \phi_1) - \phi_2 \frac{V_1}{V_2} - \phi_3 \frac{V_1}{V_3} + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{23} \frac{V_1}{V_2} \phi_2\phi_3 \right] \quad (10)$$

$$J_2 = -\phi_2 D_2(\phi_1,\phi_2) \frac{d}{dx} \left[\ln \phi_2 + (1 - \phi_2) - \phi_1 \frac{V_2}{V_1} - \phi_3 \frac{V_2}{V_3} + (\chi_{12}\phi_1 \frac{V_2}{V_1} + \chi_{23}\phi_3)(\phi_1 + \phi_3) - \chi_{13} \frac{V_2}{V_1} \phi_1\phi_3 \right] \quad (11)$$

Equations (10) and (11) are two coupled non-linear differential equations which have to be solved numerically. One should realize that eqns. (10) and (11) are simplified phenomenological relations. Although it seems that both components will diffuse independently, this is not true. One can see from eqns. (8) and (9) (or from eqns. (10) and (11)) that the activity of component 1 is not only dependent on its concentration but also on the concentration of components 2 and 3 and on the interaction parameters between components 1 and 2 (χ_{12}), 1 and 3 (χ_{13}) and 2 and 3 (χ_{23}). Secondly, the diffusion coefficient, D_1, is concentration dependent, not only on the concentration of component 1 but also on the concentration of component 2, because in the case of a liquid mixture both components will exert a plasticizing action and the diffusion coefficients will be enhanced by the combined action. The concentrations of components 1 and 2 change continuously from upstream to downstream phase during steady-state transport. Because the diffusion coefficients are assumed to be concentration dependent they will also change accordingly across the membrane as a function of the distance.

Evaluation of the binary interaction parameter χ_{12}

Solutions involving hydrogen bonding show deviations from ideal behaviour, especially in mixtures of liquids with strong hydrogen bonding such as water and ethanol.

A measure for the deviation from ideality is given by the excess functions. In Fig. 1 the enthalpy, ΔH_m, excess entropy, ΔS^E, and excess free energy of mixing, ΔG^E, of the system ethanol—water are given [17]. One can see from Fig. 1 that the excess functions are strongly concentration dependent. The χ_{12} parameter, which is in fact a free energy parameter, can be determined from the excess free energy of mixing data, ΔG^E. Using Flory—Huggins thermodynamics [16], χ_{12} is given by

$$\chi_{12} = \frac{1}{m_1 v_2}\left[m_1 \ln\frac{m_1}{v_1} + m_2 \ln\frac{m_2}{v_2} + \frac{\Delta G^E}{RT}\right] \tag{12}$$

From eqn. (12), χ_{12} can be calculated as a function of v when data on ΔG^E are available. This method of calculating χ_{12} values has been used by several authors [18, 19].

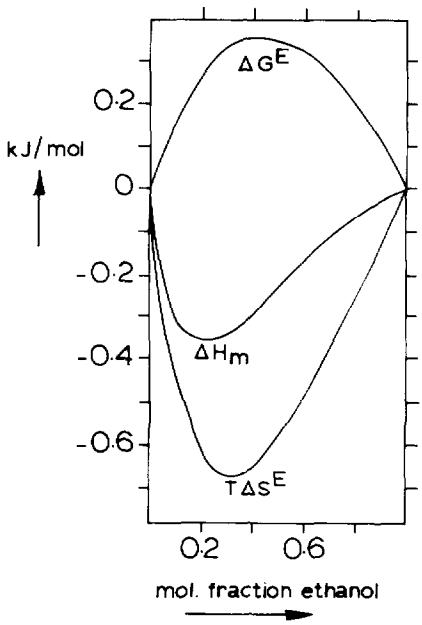

Fig. 1. Excess functions of ethanol—water mixtures at 25°C [17].

Dondos [20] used another equation for calculating the χ_{12} parameter:

$$\chi_{12} = \frac{\Delta G^E}{RT\, m_1\, m_2} \tag{13}$$

Equations (12) and (13) are equal when the molar volumes of components 1 and 2 are the same. In the case of water and ethanol the ratio of the molar volumes is far from unity. The binary interaction parameter χ_{12}, calculated from eqns. (12) and (13), is given in Table 1. It is striking that χ_{12}, when cal-

culated from eqn. (12), decreases as a function of the volume fraction of water while, when calculated from eqn. (13), χ_{12} increases.

Because eqn. (12) accounts for differences in molar volumes, we will use the χ_{12} values calculated from this equation. These values are represented in Fig. 2. From Table 1 and Fig. 2 it is clear that the χ_{12} parameter is concentration dependent; a fourth grade polynomial relation has been chosen to express the $\chi_{12}(v)$ function. The coefficients were found by using a least squares method; they are given in Table 2.

TABLE 1

Binary interaction parameters for ethanol—water mixtures calculated from eqns. (12) and (13); the concentrations are given in volume fractions

Water v_1	Ethanol v_2	ΔG^E [a] (J·mol^{-1})	χ_{12}	
			eqn. (12)	eqn. (13)
0.74	0.26	293	0.86	1.34
0.55	0.45	498	0.95	1.28
0.42	0.58	648	1.05	1.27
0.32	0.68	729	1.14	1.25
0.24	0.76	720	1.20	1.18
0.17	0.83	643	1.24	1.10
0.12	0.88	546	1.30	1.07
0.07	0.93	388	1.32	1.00
0.03	0.97	204	1.34	0.93

[a]From Ref. [21].

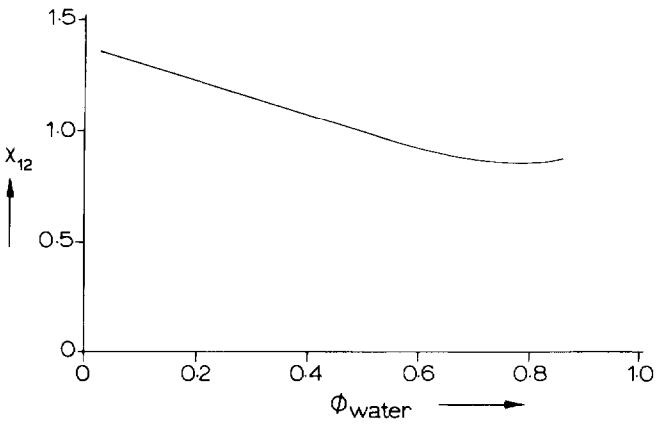

Fig. 2. Interaction parameter, χ_{12}, for ethanol—water as a function of the volume fraction of water.

TABLE 2

Coefficients for the functions $\chi_{12}(v_2)$ or $\chi_{12}(u_2)$

$\chi_{12} = a + b\,v_2 + c\,v_2^2 + d\,v_2^3 + e\,v_2^4$

a	b	c	d	e
0.98	−1.35	4.15	−3.31	0.89

v_2: Volume fraction of ethanol in ethanol—water mixtures.
u_2: Volume fraction of ethanol referred to the nonsolvent part in the ternary system.

Evaluation of the binary parameters χ_{13} and χ_{23}

Two methods are available to determine interaction parameters of a polymer and a nonsolvent: equilibrium swelling experiments and inverse gas chromatography. The disadvantage of the latter method is that interaction parameters are obtained for infinite polymer concentrations, χ^{∞}, at elevated temperatures. Because the interaction parameter is usually temperature and concentration dependent, extrapolation is often difficult. Swelling experiments are easy to perform at any temperature. The extent of swelling depends on the interaction between polymer and penetrant (in our case the nonsolvent). Polymers, applied as homogeneous or dense membranes as in pervaporation experiments, absorb only a small quantity of nonsolvent. The membrane can be considered as a swollen gel or a network with crosslinks caused by crystalline regions, chain entanglements or Van der Waals interactions. The swelling behaviour of such a network can be expressed by the Flory—Rehner theory [16]. The free energy change, ΔG, involved in the mixing of a nonsolvent and a polymer consists of two parts, the free energy of mixing, ΔG_m, and the elastic free energy, ΔG_{el}, [16]:

$$\Delta G = \Delta G_m + \Delta G_{el} \tag{14}$$

At swelling equilibrium, $\Delta G = 0$, eqn. (15) is obtained:

$$\ln(1 - v_p) + v_p + \chi v_p^2 + \frac{V_1}{\overline{M}_c \bar{v}_p}\left(v_p^{1/3} - \frac{1}{2} v_p\right) = 0 \tag{15}$$

$\overline{M}_c$ can be interpreted as the average molecular weight between two crosslinks. In polymer—nonsolvent systems with small amounts of nonsolvent in the polymer, the last term in eqn. (15) can be neglected. In the case of cellulose acetate the values of χ will not differ by more than 0.05, even for very unrealistic values of $\overline{M}_c$ ($\overline{M}_c$ = 265, the molecular weight of one segment). This is within the accuracy of the experimentally determined values. Equation (15) has thus been reduced to a very simple form:

$$\chi = -\frac{[\ln(1 - v_p) + v_p]}{v_p^2} \tag{16}$$

The results of the swelling experiments are given in Table 3. The solubility of water in cellulose acetate is in close agreement with values obtained by other investigators [13, 22]. For the calculations of the profiles, the χ_{13} and χ_{23} parameters have been considered as constant.

TABLE 3

Sorption values and binary interaction parameters of cellulose acetate/water and cellulose acetate/ethanol

	Solubility (g penetrant/ 100 g dry polymer)	Weight fraction penetrant	Volume fraction penetrant	χ
CA/water	14.3	0.125	0.157	1.4
CA/ethanol	21.5	0.177	0.262	1.1

Calculation of concentration profiles

In order to calculate concentration profiles the following approach has been followed. A homogeneous membrane is divided into a number of infinitesimally thin layers [23—25]. The fluxes, J_1 and J_2, across every layer are the same because of the steady-state condition. Since the concentration difference over a thin layer is small, linear relations can be written between fluxes and forces. The intensive variables (i.e., chemical potentials) change continuously from the feed across the membrane to the permeate side. Equilibrium exists at the hypothetical interfaces of the thin layers; therefore the chemical potential of a component at the outstream side of the nth layer is equal to that at the instream side of the $(n+1)$th layer.

In cases where the concentration profiles in the membrane are far from linear one can question if it is permissible to use linear relations, because a small number of layers is responsible for the major part of the concentration difference. In such a case the membrane has to be divided into a large number of layers so that the concentration difference over any single layer is small. By using a large number of layers ($n > 100$) of equal thickness, results of the calculation procedure become independent of this number, which is an indication that the procedure followed is correct.

An alternative procedure, as suggested by McCallum [25], is to divide the membrane into a number of layers of equal concentration difference but of unequal thickness. With this procedure it is also possible to treat non-linear behaviour, but the computation is more complex than the procedure we applied. By taking each layer to be infinitesimally thin, it is assumed that the concentration gradient across a layer is equal to the concentration difference over the layer divided by its thickness:

$$\frac{d\phi}{dx} \equiv \frac{\phi_{x+\Delta x} - \phi_x}{\Delta x} \tag{17}$$

The transport equations (10) and (11) can be applied to each of the layers. When eqn. (17) is substituted into eqns. (10) and (11), two coupled non-linear differential equations have been transformed into two non-linear equations with two variables, ϕ_1 and ϕ_2. It is also possible to transform these non-linear equations into linear equations, by expressing ln a_1 and ln a_2 as total differentials of ϕ_1 and ϕ_2. After substitution, eqn. (5) becomes

$$J_1 = -\phi_1 D_1 \frac{\mathrm{d} \ln a_1}{\mathrm{d}x} = -\phi_1 D_1 \left[\frac{\partial \ln a_1}{\partial \phi_1} \frac{\mathrm{d}\phi_1}{\mathrm{d}x} + \frac{\partial \ln a_1}{\partial \phi_2} \frac{\mathrm{d}\phi_2}{\mathrm{d}x} \right] \tag{18}$$

$$J_2 = -\phi_2 D_2 \frac{\mathrm{d} \ln a_2}{\mathrm{d}x} = -\phi_2 D_2 \left[\frac{\partial \ln a_2}{\partial \phi_1} \frac{\mathrm{d}\phi_1}{\mathrm{d}x} + \frac{\partial \ln a_2}{\partial \phi_2} \frac{\mathrm{d}\phi_2}{\mathrm{d}x} \right] \tag{19}$$

The partial derivatives $\partial \ln a_1/\partial \phi_1$, $\partial \ln a_1/\partial \phi_2$, $\partial \ln a_2/\partial \phi_1$ and $\partial \ln a_2/\partial \phi_2$ can be obtained by differentiating eqns. (8) and (9) to ϕ_1 and ϕ_2 respectively (see Appendix). The result is two linear equations for J_1 and J_2 with two variables ϕ_1 and ϕ_2:

$$J_1 = -\frac{\phi_1(n-1)D_1(\phi_1,\phi_2)}{\Delta x} \{g_{11}[\phi_1(n) - \phi_1(n-1)] + g_{12}[\phi_2(n) - \phi_2(n-1)]\} \tag{20}$$

$$J_2 = -\frac{\phi_2(n-1)D_2(\phi_1,\phi_2)}{\Delta x} \{g_{21}[\phi_1(n) - \phi_1(n-1)] + g_{22}[\phi_2(n) - \phi_2(n-1)]\} \tag{21}$$

The coefficients g_{11}, g_{12}, g_{21} and g_{22} are defined in the Appendix. From eqns. (20) and (21) the concentration profiles can be calculated as follows.

When the interaction parameters χ_{12}, χ_{13} and χ_{23}, the permeation rates J_1 and J_2, the diffusion coefficients D_1 and D_2, the molar volumes V_1, V_2 and V_3 and the initial concentrations $\phi_1(n=1)$, $\phi_2(n=1)$ and $\phi_3(n=1)$ are known, the two variables $\phi_1(n=2)$ and $\phi_2(n=2)$ can be calculated. These concentrations are the starting values for the next layer. In this way we are able to calculate the concentrations ϕ_1, ϕ_2 and ϕ_3 ($\Sigma\phi_i=1$) as a function of the penetration distance.

Experimental

Materials

Cellulose acetate (E 398-3) was obtained from Eastman Chemicals. Acetone (reagent grade) was used without further purification.

Membrane preparation

Homogeneous cellulose acetate membranes were prepared by casting a solution of cellulose acetate in acetone upon a glass plate after which the acetone was allowed to evaporate in a nitrogen atmosphere. The membranes were completely transparent.

Swelling measurements

Dried strips of cellulose acetate membrane (about 0.3 g) were immersed in conical flasks containing water or ethanol. The flasks were placed in a thermostated bath at 20°C. After 24 hours the strips were removed, pressed between tissue paper and weighed in a closed flask. This procedure was continued until no further weight increase was observed. The solubility can be expressed as a relative weight increase (g penetrant/100 g dry polymer).

Pervaporation

The pervaporation experiments were carried out as described previously [26]. Vacuum at downstream side was maintained at a pressure of 13.3 Pa (0.1 mmHg) by a Crompton Parkinson vacuum pump. The pressure was measured by an Edwards piranhi. The experiments were carried out for eight hours. Samples were taken every hour and steady-state conditions were usually reached after about three hours. The thickness of the homogeneous membrane was about 20 μm. The temperature of the liquid feed mixture was about 20°C.

Product analysis

Analysis of binary ethanol—water mixtures was performed on a Varian model 3700 gas chromatograph fitted with a chromosorb 60/80 column and equipped with a thermal conductivity detector.

Results and discussion

Concentration profiles of ethanol and water in cellulose acetate membranes have been calculated using (a) apparent concentration independent diffusion coefficients calculated from steady-state pervaporation experiments, and (b) diffusion coefficients with an exponential concentration dependence.

Concentration independent diffusion coefficients

The diffusion coefficients given in the first example have been calculated from a steady-state pervaporation experiment and are in fact mean or apparent diffusion coefficients (see eqn. (22)):

$$\overline{D}_i = \frac{J_i l}{\phi_i} \tag{22}$$

These calculated values are given in Table 4, together with the permeation rates, membrane thickness and volume fractions just inside the membrane at the feed/membrane boundary. These latter values are obtained numerically from eqns. (6)—(9). From an equilibrium sorption experiment, performed under the same conditions as the pervaporation experiment, an overall sorption value of 0.34 (= volume fraction) has been obtained. This result agrees reasonably well with the calculated values of ϕ_1 and ϕ_2 given in Table 4. The

binary interaction parameters, determined as described earlier, are also given in Table 4, together with the ratios of the molar volumes which have been taken from the literature [19, 27].

TABLE 4

Parameters obtained from pervaporation experiments; feed: ethanol—water 73—27% by weight; temperature; 20°C

Pervaporation parameters	Other parameters
$J_1 = 0.033$ cm-hr^{-1}	$V_1/V_2 = 0.309$
$J_2 = 0.042$ cm-hr^{-1}	$V_1/V_3 = 0.002$
$l = 20\ \mu$m	$V_2/V_3 = 0.0065$
$\phi_1 = 0.133$	$\chi_{13} = 1.4$
$\phi_2 = 0.230$	$\chi_{23} = 1.1$
$\phi_3 = 0.637$	
$\bar{D}_1 = 13.8 \times 10^{-8}$ cm^2-sec^{-1}	
$\bar{D}_2 = 10.1 \times 10^{-8}$ cm^2-sec^{-1}	

The concentration profiles of water and ethanol in cellulose acetate have been calculated from eqns. (20) and (21), using the parameters given in Table 4. These profiles are given in Fig. 3. One can see from Fig. 3 that somewhere within the membrane the concentration of ethanol becomes zero, which is not possible. Hence, it is not correct to use transport equations for liquid mixtures such as ethanol and water, using concentration independent diffusion coefficients and uncoupled flow. This conclusion was already clear-

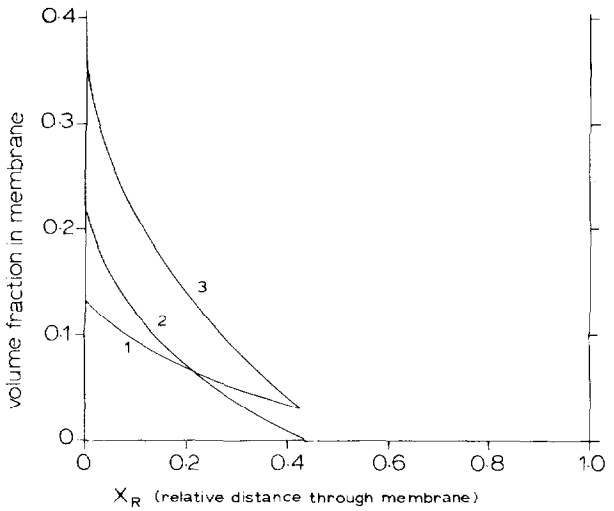

Fig. 3. Calculated concentration profiles with concentration independent diffusion coefficients obtained from steady-state pervaporation experiments 1, water; 2, ethanol; and 3, mixture; $\bar{D}_1 = 13.8 \times 10^{-8}$ cm^2/sec; $\bar{D}_2 = 10.1 \times 10^{-8}$ cm^2/sec.

ly stated by Meares [12]. In a forthcoming article [15] we will give experimental evidence for this statement. As a consequence, the model description of Lee [11] cannot be applied to this kind of liquid mixture or to any liquid mixture where the liquids exert a plasticizing action on the polymer.

The ethanol and water profiles given in Fig. 3 can be changed by increasing the diffusion coefficients. This can be carried out quite easily numerically. If the diffusion coefficients of ethanol and water increase by a factor two, while the other parameters are kept constant, profiles are obtained as given in Fig. 4. The profiles shown in Figs. 3 and 4 do not deviate much from linearity. This can be related to the fact that concentration independent diffusion coefficients have been used.

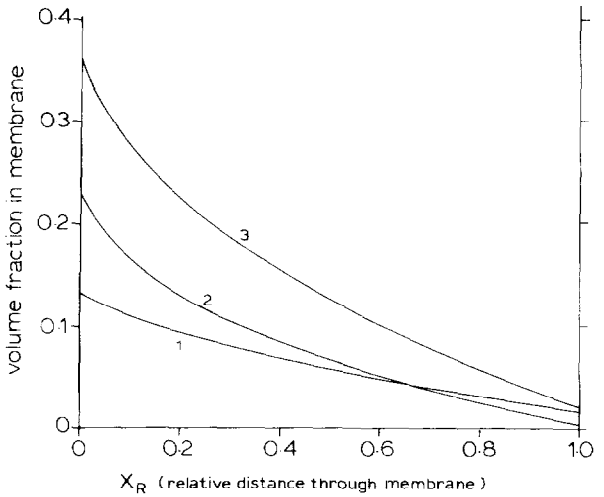

Fig. 4. Calculated concentration profiles with concentration independent diffusion coefficients. 1, water; 2, ethanol; and 3, mixture; $\bar{D}_1 = 27 \times 10^{-8}$ cm^2/sec; $\bar{D}_2 = 25 \times 10^{-8}$ cm^2/sec.

Concentration dependent diffusion coefficients

We will now consider the case of concentration dependent diffusion coefficients. Different relationships can be used to express the relation between diffusion coefficient and concentration. Most authors have used a linear [9, 28] or an exponential [2—5, 10, 29, 30] relationship. An exponential relationship holds for the case where the diffusion coefficient is more strongly concentration dependent:

$$D_i = D_{0i} \exp(\gamma_i \phi_i) \tag{23}$$

In the case of a binary mixture, the diffusion coefficients of components 1 and 2 are given by

$$D_1 = D_{01} \exp(\gamma_1 \phi_1 + \gamma_2 \phi_2) \tag{24}$$

$$D_2 = D_{02} \exp(\gamma_1 \phi_1 + \gamma_2 \phi_2) \tag{25}$$

Except for the concentration itself, two other factors determine the value of the diffusion coefficients: D_0, which is the diffusion coefficient at zero concentration of penetrant and the exponential factor, γ, which is a plasticizing constant, showing the effect of the penetrant concentration on the mobility of the penetrant in the membrane. In the case of liquid mixtures, there will be a combined plasticizing action (see eqns. (24) and (25)). For our model calculations the same values for the other parameters have been used as given in Table 4.

The influence of the proportionality factor, D_0, and the exponential factor, γ, on concentration profiles are given in Figs. 5 and 6. In Fig. 5 the proportionality factor, D_0, has been given a higher value, and in Fig. 6 a higher value is given to the exponential factor, γ. Both figures show a typical exponential behaviour. However, the curvature strongly depends on the exponential factor, γ. In Figs. 5 and 6 the exponential factor γ has the same value for both components. The actual values of γ_1 and γ_2 will not be identical because both components will not exert the same plasticizing action.

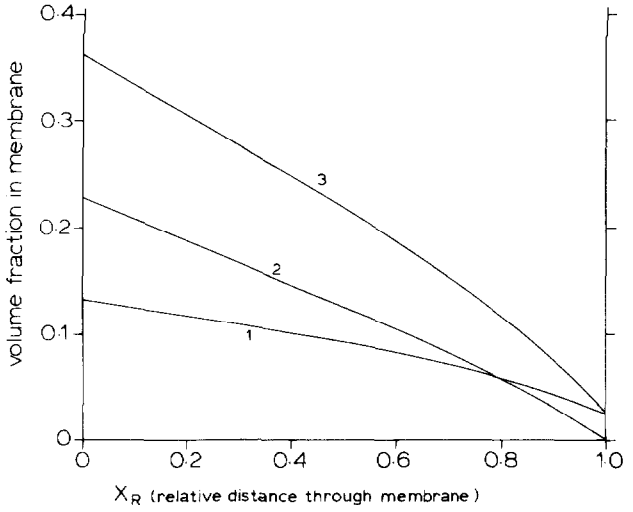

Fig. 5. Calculated concentration profiles with concentration dependent diffusion coefficients. $D_{01} = 8.8 \times 10^{-8}$ cm^2/sec; $D_{02} = 6.0 \times 10^{-8}$ cm^2/sec; $\gamma_1 = \gamma_2 = 7.3$; 1, water; 2, ethanol; and 3, mixture.

The differences between Figs. 5 and 6 are evident. If γ increases (Fig. 6), the concentration profiles become more concave. This is not unexpected since the contribution of the exponential factor is more important than that of the proportionality factor, D_0. The exponential factor γ is undoubtedly related to the Flory–Huggins interaction parameter, so for the system water/ethanol/cellulose acetate, γ_2 (ethanol) will have a higher value than γ_1 (water).

At this stage a more precise study of the influence of the different factors (D_0, γ) on the concentration profile did not seem relevant to us without detailed information about experimental concentration profiles. In a forth-

coming article [15] we will report on experimental concentration profiles of different binary mixtures in polymeric membranes. Diffusion coefficients will be calculated according to the model described in this article.

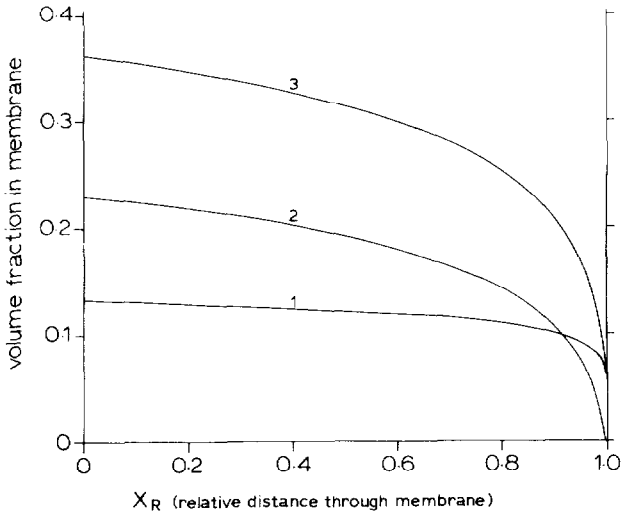

Fig. 6. Calculated concentration profiles with concentration dependent diffusion coefficients. $D_{01} = 7.0 \times 10^{-9}$ cm^2/sec; $D_{02} = 1.1 \times 10^{-9}$ cm^2/sec; $\gamma_1 = \gamma_2 = 20.78$; 1, water; 2, ethanol; and 3, mixture.

Conclusions

- A modified solution—diffusion model has been developed which describes the transport of liquid mixtures through homogeneous membranes. In the present study, transport of ethanol—water through cellulose acetate membranes has been investigated.
- The model takes into account coupling in the thermodynamic part as well as in the diffusive part of the transport equations.
- Transport of aqueous mixtures cannot be described with a concentration independent diffusion coefficient.

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List of symbols

a	Activity
B	Mobility (mmol-sec^{-1}-N^{-1})
D	Diffusion coefficient (cm^2-sec^{-1})

$\bar{D}$ Mean or apparent diffusion coefficient (cm^2-sec^{-1})
D_0 Diffusion coefficient at zero concentration (cm^2-sec^{-1})
ΔG_m Free energy of mixing (J-mol^{-1})
ΔG^E Excess free energy of mixing (J-mol^{-1})
J Permeation rate (cm-hr^{-1})
l Membrane thickness (μm)
m Mole fraction
n Number of layers
P Pressure (Pa)
R Gas constant (J-mol^{-1}-K^{-1})
T Temperature (K)
u Volume fraction referred to the nonsolvent part in the ternary system
v Volume fraction in the binary system
V Molar volume (cm^3-mol^{-1})
Δx Thickness of one layer (μm)

γ Exponential factor
χ Flory—Huggins interaction parameter
ϕ Volume fraction in the ternary system
μ Chemical potential (J-mol^{-1})
$\bar{\nu}$ Specific volume (cm^3-g^{-1})
ρ Density (g-cm^{-3})

Indices

1 Water
2 Ethanol
3 Cellulose acetate
i Component i
p Polymer

References

1 R.C. Binning, R.J. Lee, J.F. Jennings and E.C. Martin, Separation of liquid mixtures, Ind. Eng. Chem., 53 (1961) 45.
2 S.N. Kim and K. Kammermeyer, Actual concentration profiles in membrane separation, Sep. Sci., 5 (1970) 679.
3 R.Y.M. Huang and V.J.C. Lin, Separation of liquid mixtures by using polymer membranes. 1. Permeation of binary organic liquid mixtures through polyethylene, J. Appl. Polym. Sci., 12 (1968) 2615.
4 R.B. Long, Liquid permeation through plastic films, Ind. Eng. Chem. Fundam., 4 (1965) 445.
5 P. Aptel, J. Cuny, J. Jozefowicz, G. Morel and J. Neel, Liquid transport through membranes prepared by grafting of polar monomers onto poly(tetrafluoroethylene) films. II. Some factors determining pervaporation rate and selectivity, J. Appl. Polym. Sci., 18 (1974) 351.
6 M. Fels and R.Y.M. Huang, The effect of styrene grafting on the diffusion and solubility of organic liquids in polyethylene, J. Appl. Polym. Sci., 14 (1970) 537.

7 D.R. Paul and O.M. Ebra-Lima, The mechanism of liquid transport through swollen polymer membranes, J. Appl. Polym. Sci., 15 (1971) 2199.
8 M. Fels, Permeation and separation behavior of binary organic mixtures in polyethylene, AIChE Symp. Ser., 68 (1972) 49.
9 F.W. Greenlaw, R.A. Shelden and E.V. Thompson, Dependence of diffusive permeation rates on upstream and downstream pressures. II. Two component permeant, J. Membrane Sci., 2 (1977) 333.
10 R.W.M. Tock, J.Yu. Cheung and R.L. Cook, Dioxane—water transport through Nylon-6 membranes, Sep. Sci., 9 (1974) 361.
11 C.H. Lee, Theory of reverse osmosis and some other membrane permeation operations, J. Appl. Polym. Sci., 19 (1975) 83.
12 P. Meares, Transport through polymer membranes from the liquid phase, Ber. Bunsenges. Phys. Chem., 83 (1979) 342.
13 H.K. Lonsdale, U. Merten and R.L. Riley, Transport properties of cellulose acetate osmotic membranes, J. Appl. Polym. Sci., 9 (1965) 1341.
14 U. Merten, Transport properties of osmotic membranes, in: U. Merten (Ed.), Desalination by Reverse Osmosis, The M.I.T. Press, Cambridge, Mass., 1966, p. 15.
15 M.H.V. Mulder, T. Franken and C.A. Smolders, On the separation of ethanol/water mixtures by pervaporation. II. Experimental concentration profiles, submitted to J. Membrane Sci.
16 P. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.
17 A.G. Mitchell and W.F.K. Wynne-Jones, Thermodynamic and other properties of solutions involving hydrogen bonding, Disc. Faraday Soc., 15 (1953) 161.
18 T.M. Aminabhavi and P. Munk, Preferential adsorption onto polystyrene in mixed solvent systems, Macromolecules, 12 (1979) 607.
19 F.W. Altena and C.A. Smolders, Calculation of liquid—liquid phase separation in a tenary system of a polymer in a mixture of a solvent and a nonsolvent, Macromolecules, 15 (1982) 1491.
20 A. Dondos, P. Rempp and H. Benoit, Effet des propriétés thermodynamiques des mélanges de solvants sur les dimensions de chaines macromoléculaires, J. Polym. Sci., Part C, 30 (1970) 9.
21 S. Westmeier, Excessenthalpie, Freie Excessenthalpie, Excessvolumen und Viskosität von Ausgewählten binären flüssigen Mischungen. Teil II. Die Systeme Wasser—Methanol und Wasser—Äthanol, Chem. Techn., 28 (1976) 350.
22 M.A. Frommer, M. Shporer and R.M. Messalem, Water binding and irreversible dehydration processes in cellulose acetate membranes, J. Appl. Polym. Sci., 17 (1973) 2263.
23 O. Kedem, Water and salt transport in hyperfiltration, in: H.K. Lonsdale and H.E. Podall (Eds.), Reverse Osmosis Membrane Research, Plenum Press, New York, 1972, p. 17.
24 K.S. Spiegler and O. Kedem, *Thermodynamics of hyperfiltration (reverse osmosis)* criteria for efficient membranes, Desalination, 1 (1966) 311.
25 C. McCallum and P. Meares, Computer prediction of stationary states of membranes from differential permeabilities, J. Membrane Sci., 1 (1976) 65.
26 M.H.V. Mulder, F. Kruitz and C.A. Smolders, Separation of isomeric xylenes by pervaporation through cellulose ester membranes, J. Membrane Sci., 11 (1982) 349.
27 R.C. Weast, Handbook of Chemistry and Physics, 54th Edition, CRC Press, Cleveland, Ohio, 1973—1974.
28 R. Rautenbach and R. Albrecht, Separation of organic binary mixtures by pervaporation, J. Membrane Sci., 7 (1980) 203.
29 H.W. Chandler and E.J. Henley, Diffusion and equilibrium studies for the system acrylonitrile—styrene—polyethylene, AIChE J., 7 (1961) 295.
30 D.W. McCall, Diffusion in ethylene polymers. I. Desorption kinetics for a thin slab, J. Polym. Sci., 26 (1957) 151.

Appendix

It is assumed that the binary interaction parameter, χ_{12}, is concentration dependent while the polymer—nonsolvent parameters χ_{13} and χ_{23} are considered as constant. In the case of a ternary system, χ_{12} depends only on the composition of the nonsolvent mixture in the polymer ($\chi_{12} = \chi_{12}(u_2)$).

$$u_2 = \frac{\phi_2}{\phi_1 + \phi_2} = \frac{\phi_2}{1 - \phi_3} \tag{A1}$$

For the $\chi_{12}(u_2)$ function, a fourth grade polynomial relation has been chosen:

$$\chi_{12} = a + b\,u_2 + c\,u_2^2 + d\,u_2^3 + e\,u_2^4 \tag{A2}$$

The coefficients are given in Table 2. By differentiation of eqns. (8) and (9) with respect to ϕ_1 and ϕ_2, the partial derivatives $\partial \ln a_1/\partial\phi_1$, $\partial \ln a_1/\partial\phi_2$, $\partial \ln a_2/\partial\phi_1$ and $\partial \ln a_2/\partial\phi_2$ are obtained.

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) - \phi_2\left(\frac{V_1}{V_2}\right) - \phi_3\left(\frac{V_1}{V_3}\right) + (\chi_{12}(u_2)\phi_2 + \chi_{13}\phi_3)\,(\phi_2 + \phi_3)$$
$$- \chi_{23}\left(\frac{V_1}{V_2}\right)\phi_2\phi_3 - u_1 u_2 \phi_2 \frac{\partial \chi_{12}}{\partial u_2} \tag{8}$$

$$\ln a_2 = \ln \phi_2 + (1 - \phi_2) - \phi_1\left(\frac{V_2}{V_1}\right) - \phi_3\left(\frac{V_2}{V_3}\right) + (\chi_{12}(u_2)\phi_1 \frac{V_2}{V_1} + \chi_{23}\phi_3)\,(\phi_1 + \phi_3)$$
$$- \chi_{13}\left(\frac{V_2}{V_1}\right)\phi_1\phi_3 + \left(\frac{V_2}{V_1}\right) u_1^2 \phi_2 \frac{\partial \chi_{12}}{\partial u_2} \tag{9}$$

From eqns. (8) and (9) it is derived that:

$$\frac{\partial \ln a_1}{\partial \phi_1} = g_{11} = \frac{1}{\phi_1} - 1 + \frac{V_1}{V_3} - \chi_{12}\phi_2 + \chi_{23}\phi_2 \frac{V_1}{V_2} - \chi_{13}(2 - 2\phi_1 - \phi_2)$$
$$+ \phi_2(1 - \phi_1) \frac{\partial \chi_{12}}{\partial \phi_1} + u_2^2(1 - 2u_2) \frac{\partial \chi_{12}}{\partial u_2} + u_1 u_2^3 \frac{\partial^2 \chi_{12}}{\partial u_2^2} \tag{A3}$$

$$\frac{\partial \ln a_1}{\partial \phi_2} = g_{12} = -\frac{V_1}{V_2} + \frac{V_1}{V_3} + \chi_{12}(1 - \phi_1) + \chi_{13}(\phi_1 - 1)$$
$$+ \chi_{23} \frac{V_1}{V_2}(2\phi_2 + \phi_1 - 1) + \phi_2(1 - \phi_1) \frac{\partial \chi_{12}}{\partial \phi_2}$$
$$- 2u_1^2 u_2 \frac{\partial \chi_{12}}{\partial u_2} - u_1^2 u_2^2 \frac{\partial^2 \chi_{12}}{\partial u_2^2} \tag{A4}$$

$$\frac{\partial \ln a_2}{\partial \phi_1} = g_{21} = -\frac{V_2}{V_1} + \frac{V_2}{V_3} + \chi_{12}\frac{V_2}{V_1}(1-\phi_2) + \chi_{13}\frac{V_2}{V_1}(2\phi_1+\phi_2-1)$$
$$-\chi_{23}(1-\phi_2) + \frac{V_2}{V_1}\phi_1(1-\phi_2)\frac{\partial \chi_{12}}{\partial \phi_1} \qquad \text{(A5)}$$
$$+2\frac{V_2}{V_1}u_1u_2^2\frac{\partial \chi_{12}}{\partial u_2} - \frac{V_2}{V_1}u_1^2u_2^2\frac{\partial^2 \chi_{12}}{\partial u_2^2}$$

$$\frac{\partial \ln a_2}{\partial \phi_2} = g_{22} = \frac{1}{\phi_2} - 1 + \frac{V_2}{V_3} - \chi_{12}\frac{V_2}{V_1}\phi_1 + \chi_{13}\frac{V_2}{V_1}\phi_1$$
$$+\chi_{23}(2\phi_2+\phi_1-2) + \frac{V_2}{V_1}\phi_1(1-\phi_2)\frac{\partial \chi_{12}}{\partial \phi_2} \qquad \text{(A6)}$$
$$+\frac{V_2}{V_1}u_1^2(1-2u_2)\frac{\partial \chi_{12}}{\partial u_2} + \frac{V_2}{V_1}u_1^3u_2\frac{\partial^2 \chi_{12}}{\partial u_2^2}$$

The coefficients g_{11}, g_{12}, g_{21} and g_{22} have been substituted into eqns. (20) and (21).